

SIMULTANEOUS THERMOANALYTICAL and MASS SPECTROMETRIC INVESTIGATIONS
• of VOLATILE COMPOUNDS EVOLVED from MINERAL COAL up to a TEMPERATURE
RANGE of 1800 K.

K.-H. Ohrbach, A. Kettrup

Applied Chemistry, University GH Paderborn, P.O. Box 1621,
4790 Paderborn (F.R.G.)

The further development of simultaneous working coupling systems basing on different physical measuring principles is one main aspect regarding the investigation of the thermal degradation or the oxidative decomposition processes of mineral coal discussed and illustrated in this paper.

The combination of the methods "Thermogravimetry-Derivative Thermogravimetry-Differential Thermal Analysis-Mass Spectrometry" (TG-DTG-DTA-MS) using the equipment described later offers a wide variety of useful and practical applications in the field of mineral coal analysis respectively carbonaceous materials in general.

A working temperature of 1800 K and a stored temperature controlled program permit long during thermal treatment of the samples in various atmospheres as well as heating with rapid heating rates up to 20 K min⁻¹ limitation of the furnace.

For monitoring the released gases and determining the mass fragments (m/z values) a quadrupole mass spectrometer with rapid scan capability is more convenient than a time-of-flight mass spectrometer in many cases especially room saving construction, low cost, sufficient sensitivity and resolution.

Experimental Section

The coal samples were given by the "Coal Mining Research Institute" at Essen (F.R.G.). The combined thermoanalytical mass spectrometric experiments have been carried out with a coupling system consisting of Netzsch STA 429 Thermoanalyzer and Balzers Quadrupole Mass Spectrometer QMG 511.

The main instrumental feature to record mass spectra at high temperatures at standard pressure is a special constructed interface between thermoanalyzer and mass spectrometer, see Fig.1.. It permits all different experimental conditions essentially at a working pressure of 1 bar in various inert or reaction gas atmospheres at the sample introducing no complications with regard to high vacuum in the mass spectrometer. Two modes of operation depending on an interface as a pressure reduction system are possible:

1. high vacuum in the whole coupling system
2. standard pressure in different gas atmospheres in the thermoanalyzer and high vacuum $<10^{-4}$ mbar in the mass spectrometer.

Two different pressure reduction systems have been employed, alumina oxide tubes and quartz tubes with orifices at the bottom to reduce pressure in two stages. A more detailed description has been given earlier (1).

High vacuum has been the preferred method to get higher ion yields in the upper mass range avoiding fragmentation of evolved compounds. The storage of twelve different mass units (mass ranges) up to m/z values of 511 including all adjustable instrumental parameters is possible. The scan speed varies between 0.1 ms to 30 s per mass unit.

For the DTA experiments a measuring range of 0.05 mV full scale has been applied with constant heating rates of 10 K min⁻¹.

Magnesium oxide has been used as a reference material. We have chosen it as a dilution substance, too, when heating samples of particle size larger than 0.2 mm diameter so that reproducible evaluation of the DTG-DTA data can be ensured (2-7). A thermocouple Pt-Rh-Pt has been employed for temperature measuring up to 1870 K at heating rates from 0.1 to 20 (50) K applying various temperature programs in the DTA measuring range from 0.05 to 100 mV. The sample mass was taken with 10 mg and the DTG sensitivity 0.5 mg/min cm.

Results

Investigations of coal pyrolysis, pyrolysis kinetics respectively new trend analysis which is done regarding coal rank have been intensively described by several authors in view of determination of coal structure or the devolatilization process study (8-11). This series of experiments which are reported here leads to the identification of time temperature dependent coal devolatilization products simultaneously. Referring to our preliminary studies into metal complexes our interest has mainly been aimed to apply this coupling system in the field of coal analysis, e.g. evolved gas analysis. Regarding gasification process control the utilization of this equipment may permit realistic experimental conditions such as temperature, time and atmosphere similar to a gasification environment. We gained our experience by exemplarily investigating a few standard coal samples to test the capability of the apparatus as a possible use in devolatilization analysis.

The TG-DTG-DTA data correlate reasonably. Gas evolution of a sample results in mass loss accompanied by thermal effects exhibited as peak width, -height, -area in the DTG (DTA) curve as illustrated in Fig. 2. The increase in pressure as well as the temperature can be recorded and measured at the sample. The data obtained by our thermoanalytical investigations have not shown striking characteristics or significant trends with respect to coal rank as sometimes reported in the literature. This is possibly due to altering the representative samples e.g. the sensitivity for reproducing the data. Before generalizing these vacuum results additional tests have been performed in dynamic nitrogen and argon atmosphere showing no gradual differences, too. Table 1 shows summarized values of the DTG experiments.

Table 1

Average values of characteristic temperatures taken from the DTG curves of three standard coal samples

Coal type ^{a)} V.M. d.a.f.	^{b)} $T_{i,I}$	^{c)} $T_{f,I}$	^{d) e)} $T_{p,I}$	$T_{i,II}$	$T_{f,II}$	$T_{p,II}$
	K	K	K	K	K	K
6.9	460	588	538	-	-	-
16.2	469	576	540	727	792	752
36.3	477	571	537	673	749	707

a) coal type, volatile matter/%, b) T_i is the temperature at which the cumulative mass change reaches a magnitude that thermobalance

Resulting from our vacuum operations one striking fact seems to be very important that is to determine the gas composition of the devolatilization products in the temperature range of 1600 to 2100 K, because in our experiments we observed slightly increasing courses or maxima plateaus of ion currents when running the intensities of selected ion currents as autocontrol spectra. According to this, the begin of this phenomena is at a temperature of about 1350 K. The TG curves indicate a monotonously small decreasing mass loss. The application of a furnace working up to 2600 K for these investigations will be realized soon.

Discussion

A typical standard pressure run of a coal sample 6.9 % d.a.f. (anthracite) is shown in Fig. 2. This experiment was carried out in dynamic helium atmosphere, which is not very suitable for TG-DTA-MS measurements in general. Constant heating rates up to 1800 K and constant cooling has been employed, indicating an additional mass loss in the DTG curve. The slopes of the DTG curves were similar when nitrogen or argon were used as inert gases. In this case the sample was put on a high temperature stable ceramic plate instead of platinum crucibles. The DTG curve exhibits a sharp peak at 1721 K. Observing significant mass loss in this temperature range we have to determine the m/z values of the evolved products simultaneously beginning at temperature onsets of devolatilization to final temperatures. This mode of operation yields no DTA data but more stable TG-DTG base lines. Evolution of the gases or particles are now developed from a very large surface distribution in contrast to platinum crucibles.

It is evident that thermal properties of coal samples result in different data of mass loss corresponding to the volatile matter content. A greater amount of mass loss and unavoidably less residual products can be estimated in connection with pressure and final heating time-temperature surface distribution relationships, using the above mentioned specimen, but DTA data cannot be taken from this measuring device.

Some results concerning the different modes of operations and types of problems should be discussed exemplarily with the following examples. In Fig. 3 the TG-DTG-DTA-T-P curves of a coal sample with 36.3 % V.M. d.a.f. are shown exhibiting two peak temperatures in the DTG curve with a total mass loss of 40 %. Each step in mass loss indicated in the TG curve corresponds to an increase in pressure. The first maximum at 523 K in mass loss (endothermal slope of the DTA curve) is due to release of moisture (carbon dioxide, -monoxide equilibrium). Before reaching the second maximum temperature the mass spectrum indicates the typical breakdown pattern of homologous hydrocarbon series with increasing intensities as a function of temperature. The excitation energy applied has been 20 eV up to a mass range of 330 mass units in the temperature range from 643 to 663 K, see Fig. 4. Molecular condensation reactions cannot be excluded as well as fragmentation of higher molecular species into compounds of lower masses. In some cases we employ a rapid scan mode to observe increasing or decreasing intensities of mass fragments in a small temperature range. This is shown in Fig. 5 exhibiting the decreasing intensities of the mass range of $m/z=182$ to 184 which correspond to a release of compounds resulting from the diphenyl series accompanied by only a slight mass loss in this 10 K temperature interval. The investigations of a low volatile bituminous coal with 16.2 % V.M. d.a.f. is shown in Fig. 6, only monitoring six mass units corre-

can detect, c) T_f is the final temperature, d) T_p represents the peak temperature (12), e) I, II correspond to the first (second) mass change.

In our investigations the optimum instrumental parameters have been constant to give comparable and reproducible results. The evaluation especially the mass spectrometric data are labour-intensive and time consuming. A complete computing system RT-11 (Digital Equipment Corporation) compatible to the combined TG-DTA-MS apparatus is available and will be applied to resolve these problems soon.

The material for the most common crucibles used for TG-DTA measurements is alumina oxide, but platinum respectively tantalum has been tested in our laboratory. The yield of the evolved gases has been predicted as much higher by use of metal crucibles due to catalytic effects of Pt or Ta, but in our tests we did not observe a drastic change in gas composition or TG-DTA results by inserting constant masses of 10 mg of each coal sample and employing constant heating rates of 10 K/min.

In all runs we registered a great number of possible fragments from the macromolecular structure broken into smaller pieces. The abundance of ions in the upper mass range released from coal at higher temperatures decreases due to thermal decomposition of the species prior to ionization. The yield of fragment ions above 250 mass units increases with decreasing excitation energy at 20 eV, see Fig. 2. Thermally activated compounds always need less energy for decomposition than "cold" particles. This effect is prevailing when examining the fragmentation pattern of aliphatic molecules in contrast to aromatic devolatilization products. The influence of increasing temperature on the decomposition of the volatiles cannot be elucidated at present as well as secondary reactions of the tar when performing high vacuum analysis.

The mass fragments of structural related compounds have been monitored recording selected ion currents of different hydrocarbon series including mass values of heterocycles (sulfur and nitrogen containing compounds). Previous work has been done by Meuzelaar et al. (12). We have observed great amounts of stable polycyclic aromatic series with one or more maxima at different temperatures and the occurrence of double charged positive ions as shown in Fig. 3. The typical fragmentation of alkylated benzene series has been detected in every case indicated by loss of the homologous mass unit 14. The large number of data of our experiments has to be processed on-line by the above mentioned computing system.

The yield of the devolatilization products within heating periods depends little on heating rates when coals of similar rank are investigated, but on particle size and surrounding atmosphere respectively pressure with regard to detectable fragment ions into the mass spectrometer. The experimental conditions using the high temperature stable ceramic gas inlet system in static air or employing dynamic air flow without pressure-temperature corrections during the experiment result in non reproducible mass spectral data. Small heating rates of below 5 K/min cause more rapid oxidation of the volatiles released. Accordingly the intensities of the degradation products in the low mass range show an increase corresponding to exothermal effects in the DTA curve. The peak temperatures of the DTA curves correlate with maxima in derivative thermogravimetric and pressure curves. Therefore, most of our experiments were run in vacuum. It must be mentioned that at high temperatures the volatiles may undergo radical reactions which cannot be observed by use of the mass spectrometer.

sponding to the cleavage products indicated exceptionally sulfur containing molecules in the lower mass range of interest. The evolution of BTX-aromatic compounds exhibits a maximum intensity at 723 K as well as other polycyclic aromatic substances. Experiments observing the egress rates of the volatiles released are projected.

Conclusion

Summarizing the goals of our investigations there are two categories of interest dealing on the one hand with the application of none computerized TG-DTG-DTA-MS analysis and on the other hand with complete on-line control of the devolatilization process in a high temperature furnace above 1800 K. The first directly offers the possibility to get unreliable data to study thermal decomposition of carbonaceous material with regard to gas composition depending on temperature-time relationships employing different atmospheres and standard pressure. The second object is to quantify these results and data to study the kinetics during thermal degradation up to higher mass ranges and temperatures. Practical application must be a main feature of these investigations. Because coal structure and the corresponding thermal decomposition process cannot be separated. Therefore the tests have to be carried out simultaneously not basing on mathematical description of pyrolysis behaviour of model substances which are often far away from practical utilization.

The enhancement of the abundance of mass fragments is influenced by catalytic effects of transition metal compounds. We are engaged to study these effects during our continuous work as well as reactions of tar with various test gases examining the change in gas composition. The reaction gas must be introduced by use of a capillary inlet.

We conclude that additional instrumental modification of the measuring device regarding measurements related to realistic conditions and quantitative results is needed. Mass spectrometric and gas chromatographic identification of the evolved compounds after thermal treatment in the TG-DTA-MS apparatus above 1800 K would be well suited in analysis of devolatilization products.

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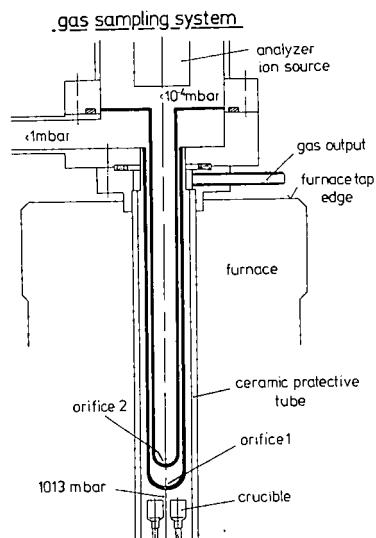


Fig. 1. Gas inlet system of the TG-DTA-MS apparatus showing two high temperature stable ceramic tubes for pressure reduction and the ceramic protective tube of the furnace.

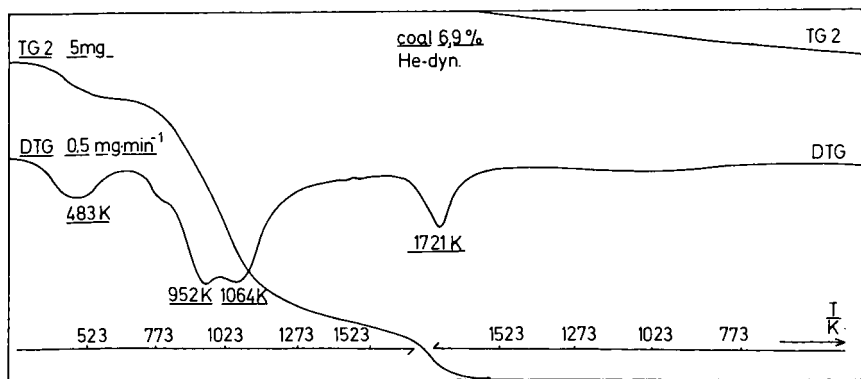


Fig. 2. The TG-DTG curves of an anthracite with 6.9 % volatile matter d.a.f. employing constant heating and cooling

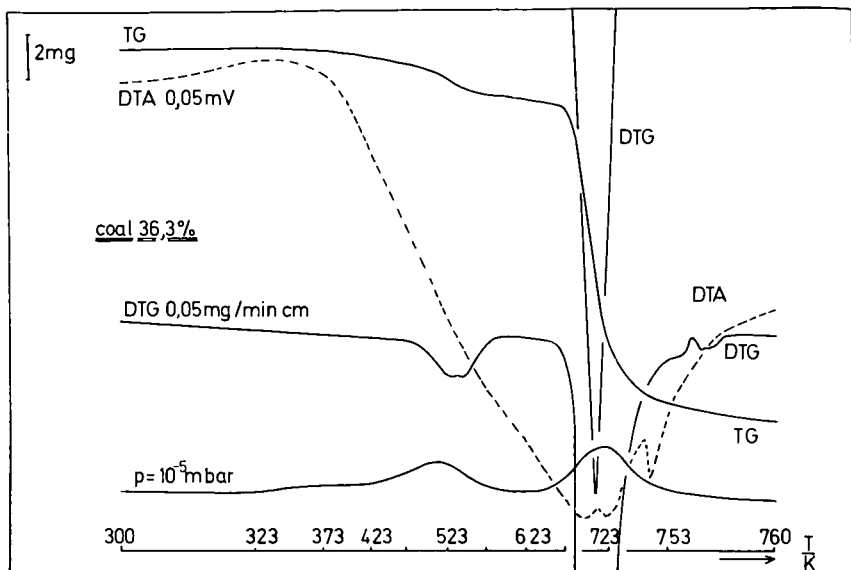


Fig. 3. TG-DTG-DTA-p-T curves of a coal sample with 36.3 % volatile matter d.a.f. recorded in high vacuum.

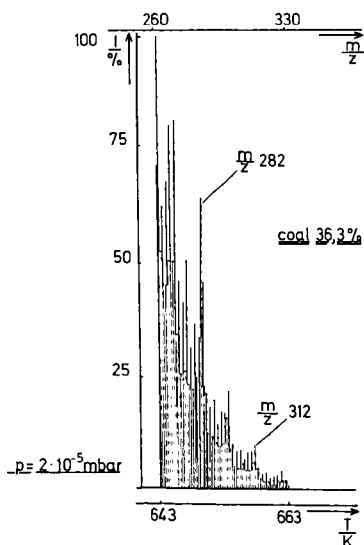


Fig. 4. Mass spectrum of a coal sample with 36.3 % volatile matter d.a.f. in the temperature range from 643 K to 663 K simultaneously recorded to the data mentioned in Fig. 3.

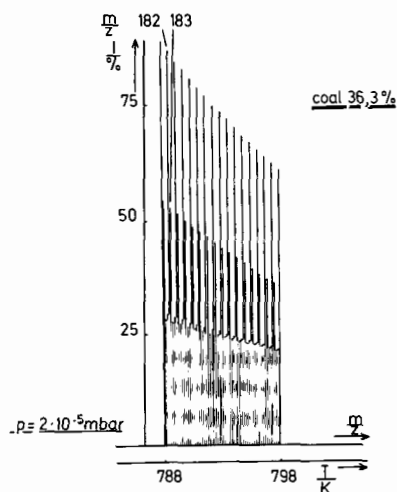


Fig. 5. Mass spectrum in the mass range from 182 to 184 mass units in the temperature range from 788 K to 798 K of a coal sample with 36.3 % volatile matter d.a.f.

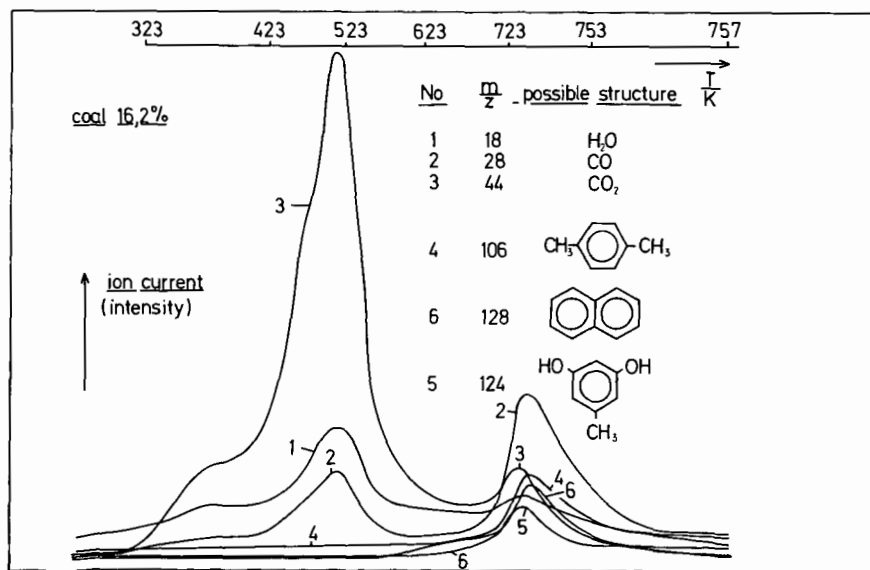


Fig. 6. Autovolt mass spectrum of five preselected ion currents corresponding to the mass fragments indicated as No. 1-5 of a coal sample with 16.2 % volatile matter d.a.f. (T-from 323 K to 757 K)